Fundamental Researches on Smelting of Sulphide Ores. IX : On the Equilibrium in the Reduction of Sulphur in Molten Tin by Hydrogen Gas

Fundamental Researches on Smelting of Sulphide Ores. IX On the Equilibrium in the Reduction of Sulphur in Molten Tin by Hydrogen Gas*

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(Received March 10, 1951)

Synopsis

In order to determine the thermodynamic properties of sulphur dissolved in molten tin, the equilibrium in the reduction of sulphur in liquid tin by hydrogen gas was investigated for the temperature range 727~873°C. It was found that the molten tin containing sulphur is regarded as an ideal solution within the limit of the experiment. Experimental results are summarized as follows:

$$\underline{S}(\text{in liq. Sn}) + H_2 = H_2S\,; \quad K = \frac{P_{H_2S}}{P_{H_2}\cdot[\%S]} = \frac{K_p}{[\%S]}\,,$$

$$\log K = -\frac{2{,}397}{T} + 0.495\,,$$

$$\Delta F^\circ = 10{,}964 - 2.264T\,.$$

Combining these equations with the published ones relating to the equilibrium constant of the formation reaction of hydrogen sulphide gas, the approximate equation expressed as a function of temperature for the dissociation pressure of sulphur dissolving in molten tin between 727° and 873°C may be represented by the following equations:

$$2\underline{S}(\text{in liq. Sn}) = S_2\,; \quad K' = \frac{P_{S_2}}{[\%S]^2}\,,$$

$$\log K' = -\frac{14{,}180}{T} + 6.090\,,$$

$$\Delta F^\circ = 64{,}860 - 27.86T\,.$$

I. Introduction

The affinity of molten tin for sulphur plays an important role when various reactions regarding to treatment of bronze vessels, e. g. temple bell or braziers, by means of copper converter, are discussed. However any datum concerning the behaviour of sulphur in molten tin at high temperatures, which gives a base for comparison between them, have not yet been published. In order to study this problem it was considered that the best way might be the employment of the following indirect method, in which thermodynamical values were computed by means of combining the equilibrium constant of reduction of the melt containing sulphur by hydrogen with the known one of dissociation reaction of hydrogen sulphide. Namely, the reaction: $\underline{S}$ (in liq. Sn) + $H_2 = H_2S$ was to be studied from thermodynamical points of view.

The equilibrium diagram of the system tin/sulphur established by Bilt and Meck-

* The 27 th report of the Research Institute of Mineral Dressing and Metallurgy.

lenburg[1] is shown in Fig. 1. According to this figure the liquid tin containing such a little amount of sulphur as studied in this report forms a homogeneous phase. Therefore applying the phase rule in the form of equation $F = C + 2 - P$, where F denotes the number of degrees of freedom, C the number of components and P the number of phases, since $C = 3$ and $P = 2$, there results $F = 3+2-2 = 3$. In the present investigation the measurements were carried out under constant pressure, i. e. 1 atm. and then the system became bi-variant. Therefore at a constant temperature when either the composition of gaseous phase or the content of sulphur in the melt was fixed, the other should have been fixed necessarily.

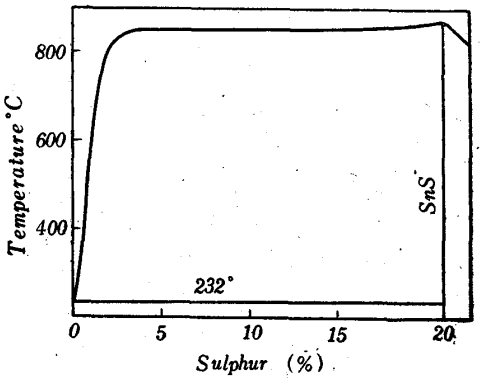

Fig. 1. Phase diagram of the System Sn–S.

In order to determine the equilibrium constant, $K = P_{H_2S}/P_{H_2}[\%S] = K_p/[\%S]$, by analyzing the sulphur in liquid phase under a certain composition of gaseous phase at constant temperature, the present experimental work was conducted.

Of course it was considered that in the case of present experiment the remarkable vaporization tendency of SnS, as pointed out in the preceding report[2], might take part in the result, but for simplicity it was not taken into account.

II. Experimental materials used

So as to prepare H_2-H_2S gas mixtures having various compositions for streaming over molten tin, considering the same points as in the case of sulphur in molten copper, the stannous sulphide powder prepared by the method described in 8 th report[2] was placed on a silica boat and under a constant temperature the H_2-H_2S gas mixture was introduced on the melt at a definite rate of flow.

Directly charging tin/stannous sulphide powder mixture into the second reaction tube, as the case of molten copper[3], seems to be large in vaporization loss of stannous sulphide from the facts that stannous sulphide has a remarkable tendency of vaporization and between the melting point of tin and of stannous sulphide a great difference is noticed, and so the Sn/S alloys containing a small amounts of sulphur made by the following procedure were used. Namely pure tin powder and the stannous sulphide powder described above were placed on a porcelain boat and inserted into the silica reaction tube, and after substituting inside with hydrogen gas, the hydrogen gas was streamed through the tube at the rate of flow: 6.97 cc/min. Then the tube was rapidly heated with an electric furnace kept at 950°C; just above the melting point of stannous sulphide, and held at the temperature for 1~2 hr. Next, the cocks of in- and out-gas tubes were closed and after removing the electric furnace

(1) W. Bilt and W. Mecklenburg, Z. anorg. allgem. Chem., 64 (1909), 231.
(2) K. Sudo, Sci. Rep. RITU, A 3 (1951), 187.
(3) K. Sudo, Sci. Rep. RITU, A 2 (1950), 519.

the tube was rapidly cooled. When cooled to room temperature the product was taken out and used for the present experiment.

The total weight of sample used in each run was about 5g.

III. Experimental apparatus and procedure

The apparatus and procedure employed were essentially same as described in 7 th report.[3] Streaming hydrogen gas on the fine powder of stannous sulphide placed on a silica boat in the first reaction tube for about an hour at 631°C and under the rate of flow: 13.7 cc/min, and the leaving gases were analyzed for hydrogen sulphide. After confirming the constancy of gas composition, the leaving gas was introduced into the second reaction tube, in which the Sn/S alloy mentioned above was placed on a porcelain boat.

Then the reaction tube was heated rapidly by an electric furnace kept at a definite elevated temperature. About 30 minutes after reaching the desired temperature, the H_2S content in leaving gas began to be analyzed so as to know the change in composition.

When the composition of gaseous phase showed a constant value, the cocks belonging to the second tube were closed to cut off the gas stream and the heating electric furnace was removed and then the reaction tube was cooled rapidly with water or ice. After cooling to room temperature the sample was then taken out and filed off into fine powder for analysis. The evolution method was used for analysis of sulphur and the result thus obtained was considered to show the content of sulphur in melt.

Of course, since in almost any case of the present experiment, the content of hydrogen sulphide in leaving gas was higher than the one in entering gas, the values observed in the case of molten copper, both values were in the same order of magnitude.

Therefore it was considered that the equilibrium might be reached immediately and the change in the content of sulphur in liquid tin caused by the difference might be almost negligible and so experiment with respect to the case, in which the content of hydrogen sulphide in entering gas was higher than the one in leaving gas, was not conducted.

IV. Experimental results

(A) The results obtained from measurements of the reduction equilibia at those temperatures, 727°, 775°, 824° and 873°C are shown in Fig. 2, 3, 4 and 5, respectively, where the gas ratio, $K_p = P_{H_2S}/P_{H_2}$, is plotted as a function of sulphur content of the melt. As can be seen from these figures, the point representing experimental results fall almost in a straight line. From these facts, it may be concluded that the melts are regarded as an ideal solution within the limit of experiment.

Therefore, from the observed data the following experimental formulas representing the variation of gas ratio, K_p, with the sulphur content of melt, [%S], are deduced.

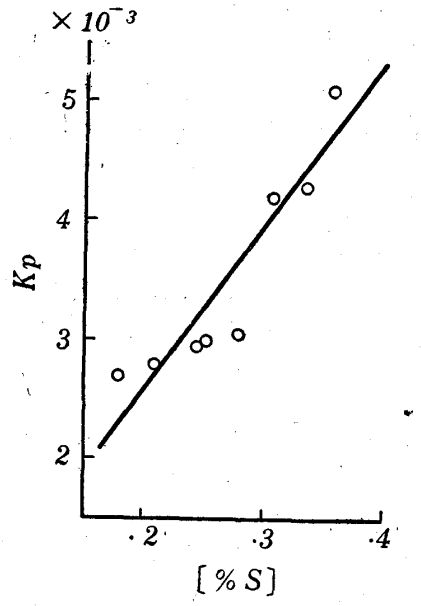

Fig. 2. Variation of sulphur in the tin with ratio of H_2S to H_2 in the gas at 727°C.

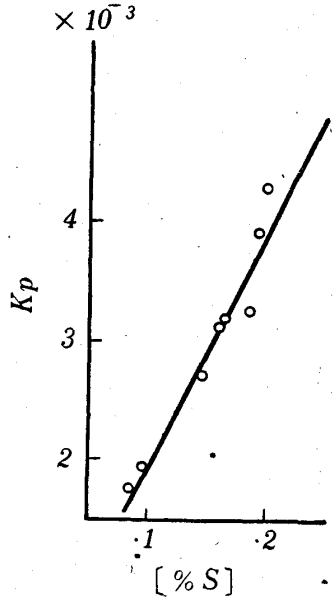

Fig. 4. Variation of sulphur in the tin with ratio of H_2S to H_2 at 824°C.

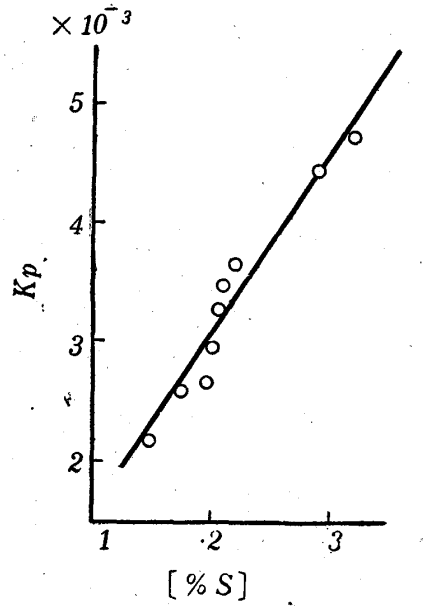

Fig. 3. Variation of sulphur in the tin with ratio of H_2S to H_2 at 775°C.

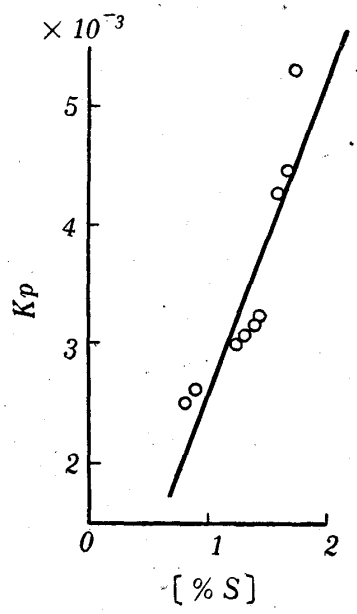

Fig. 5. Variation of sulphur in the tin with ratio of H_2S to H_2 in the gas at 873°C.

$$K_p \times 10^3 = 13.2[\%S] - 0.04 \quad \text{at 727°C} \cdots\cdots (9\cdot1)$$

$$K_p \times 10^3 = 15.1[\ //\ ] + 0.04 \quad \text{at 775°C} \cdots\cdots (9\cdot2)$$

$$K_p \times 10^3 = 19.6[\ //\ ] + 0.02 \quad \text{at 824°C} \cdots\cdots (9\cdot3)$$

$$K_p \times 10^3 = 26.6[\ //\ ] - 0.10 \quad \text{at 873°C} \cdots\cdots (9\cdot4)$$

By the way the conditions and the results of these experiments are given in Table 1.

(B) Correlation between equilibrium constant and temperature

The values of equilibrium constant, $K=K_p/[\%S]$, of the reactions $\underline{S}$(in liq. Sn)$+H_2=H_2S$, at each temperature calculated from the observed values are given in Table 2. Plots of the logarithmic value of equilibrium constant against the reciprocal of

Table 1. Experimental conditions and results obtained.

Run	Rate of flow cc/min	Temp. ℃	$P_{H_2S}/P_{H_2}\times10^3$		S in the melt %	$K=P_{H_2S}/P_{H_2}\cdot[\%S]\times10^2$
			Entering	Leaving		
1	13.7	727	2.52	2.69	0.179	1.50
2	〃	〃	〃	2.83	0.207	1.37
3	〃	〃	〃	2.96	0.246	1.20
4	〃	〃	〃	3.01	0.251	1.20
5	〃	〃	〃	3.04	0.282	1.08
6	〃	〃	〃	4.19	0.307	1.37
7	〃	〃	〃	4.28	0.335	1.28
8	〃	〃	〃	5.11	0.356	1.43
9	〃	775	〃	2.19	0.147	1.49
10	〃	〃	〃	2.62	0.172	1.52
11	〃	〃	〃	2.64	0.194	1.36
12	〃	〃	〃	2.96	0.199	1.49
13	〃	〃	〃	3.25	0.207	1.57
14	〃	〃	〃	3.47	0.210	1.65
15	〃	〃	〃	3.64	0.220	1.65
16	〃	〃	〃	4.45	0.290	1.54
17	〃	〃	〃	4.73	0.321	1.47
18	〃	824	〃	1.76	0.085	2.07
19	〃	〃	〃	1.96	0.094	2.08
20	〃	〃	〃	2.73	0.145	1.88
21	〃	〃	〃	3.13	0.160	1.95
22	〃	〃	〃	3.20	0.166	1.93
23	〃	〃	〃	3.27	0.185	1.77
24	〃	〃	〃	3.93	0.192	2.05
25	〃	〃	〃	4.31	0.201	2.14
26	〃	873	〃	2.49	0.083	3.00
27	〃	〃	〃	2.58	0.090	2.87
28	〃	〃	〃	2.99	0.125	2.39
29	〃	〃	〃	3.05	0.131	2.33
30	〃	〃	〃	3.14	0.140	2.24
31	〃	〃	〃	3.18	0.143	2.22
32	〃	〃	〃	4.25	0.159	2.67
33	〃	〃	〃	4.45	0.168	2.65
34	〃	〃	〃	5.30	0.174	3.05

Table 2. Equilibrium constants at various temperatures in the reaction: $\underline{S}$(in liq. Sn) $+ H_2 = H_2S$, $K = P_{H_2S}/P_{H_2}\cdot[\%S]$.

Temperature ℃		727	775	824	873
Temperature abs.		1,000	1,048	1,097	1,145
$1/T\times10^4$		10.00	9.54	9.12	8.73
$K\times10^2$		1.32	1.51	1.96	2.66
$-\log K$	(exp.)	1.879	1.821	1.708	1.575
	(9·5)	1.902	1.792	1.689	1.598

the absolute temperature are shown in Fig. 6. In the light of this figure, it is known that the correlation between them is linear functional. This linear equation is as follows:

$\underline{S}$(in liq. Sn) + $H_2 = H_2S$;

$$K = K_p/[\%S] ,$$

$$\log K = -\frac{2,397}{T}+0.495 . \quad \cdots\cdots (9\cdot5)$$

The values of $\log K$ at each experimental temperature computed from the above equation are given in Table 2 and they agree with the observed ones.

The corresponding equation for the standard free energy change in the reaction is

$$\Delta F^\circ = 10,964 - 2.264\,T . \quad \cdots\cdots\cdots (9\cdot6)$$

On the other hand, equation (9·5) is rewritten as follows:

$$\log K_p - \log [\%S] + \frac{2,397}{T} - 0.495 = 0 . \quad \cdots\cdots\cdots (9\cdot7)$$

That is, when $\log K_p$, $\log[\%S]$ and $1/T$ are denoted on three axes in cubic system respectively, the equation represents a plane. The relation between them is shown in Fig. 7.

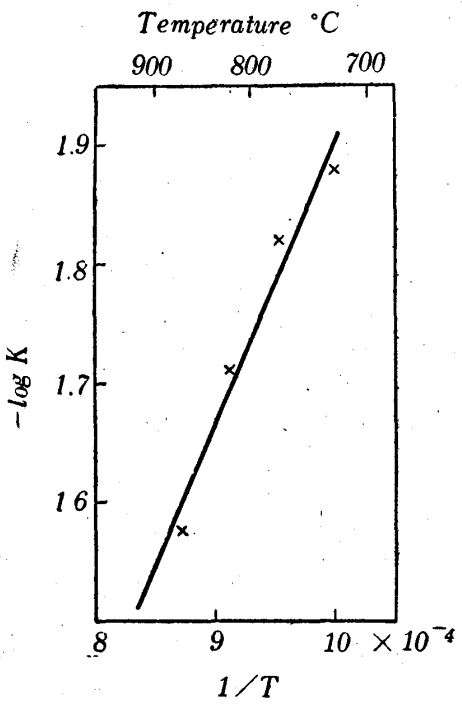

Fig. 6. Correlation between log K and temperature.

$$K = \frac{P_{H_2S}}{P_{H_2}\cdot[\%S]}$$

V. Dissociation pressure of sulphur in molten tin

(A) Combining the approximate equation for the reduction equilibrium of sulphur in liquid tin mentioned above with equation (1·2) for the formation reaction of hydrogen sulphide gas, the following approximate formula was obtained for representing the variation of dissociation pressure of sulphur in molten tin with the reciprocal of absolute temperature.

$2\underline{S}$ (in liq. Sn) $= S_2$; $K' = P_{S_2}/[\%S]^2$,

$$\log K' = -\frac{14,180}{T}+6.090 \quad \cdots\cdots (9\cdot8)$$

The values of $\log K'$ at each experimental temperature computed from this equation are given in Table 3(I).

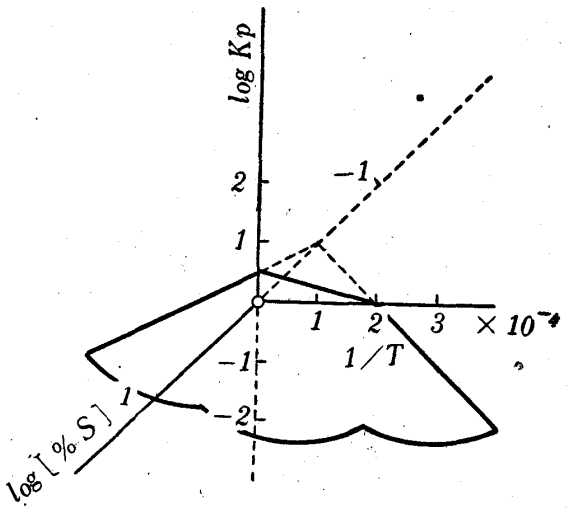

Fig. 7. Relation among log K_p, log[%S] and $1/T$.

Table 3. Equilibrium constants at various temperatures in the reaction: $2\underline{S}(\text{in liq. Sn}) = S_2$, $K' = P_{S_2}/[\%S]^2$.

Temperature °C		727	775	824	873
-log K		1.879	1.821	1.708	1.575
-log D_{H_2S}		4.277	3.854	3.463	3.099
-log K'	(I)	8.090	7.438	6.828	6.289
	(II)	8.035	7.496	6.879	6.249

Furthermore, the corresponding equation for the standard free energy change in the dissociation reaction is

$$\Delta F^\circ = 64{,}860 - 27.86\,T\,. \quad \cdots\cdots (9\cdot9)$$

Moreover, equation (9·8) is also rewritten as follows:

$$\log P_{S_2} = 2\log[\%S] + \frac{14{,}180}{T} - 6.090 = 0\,. \quad \cdots\cdots (9\cdot10)$$

That is, when $\log P_{S_2}$, $\log[\%S]$ and $1/T$ are denoted on three axes in cubic system respectively, this equation represents a plane as shown in Fig. 8.

(B) The values of $\log K'$ at each temperature obtained by combining the results observed in above experiments with the corresponding ones to the dissociation equilibrium of hydrogen sulphide gas calculated from equation (1·6) are given in Table 3(II).

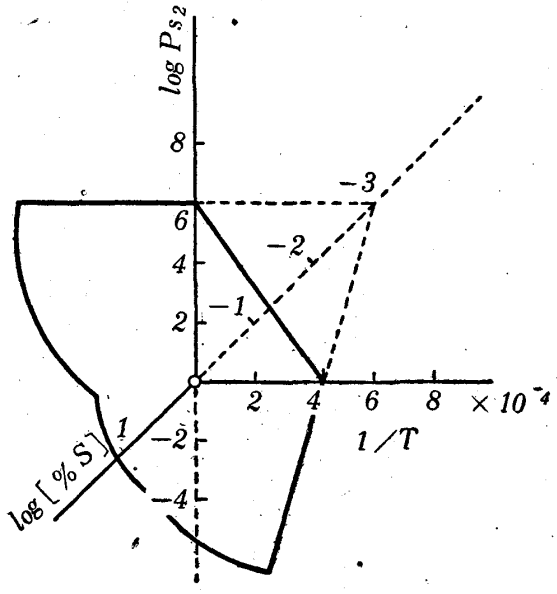

Fig. 8. Relation among $\log P_{S_2}$, [%S] and $1/T$.

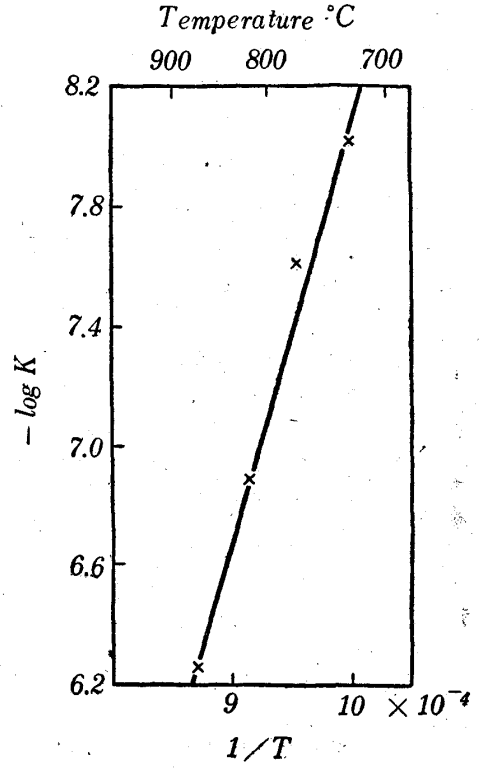

Fig. 9. Correlation between $\log K'$ and temperature. $K' = P_{S_2}/[\%S]^2$

As can be seen in Table 3, the values of log K' obtained by these two procedures agree with each other. That is, it is known that the approximate equation (9·8) is sufficient to represent the results.

When the values of log K' mentioned above are plotted against the reciprocal of the absolute temperature, a straight line is obtained as shown in Fig. 9.

Summary

The equilibrium in the reduction of sulphur in molten tin by hydrogen gas was studied at temperatures between 727° and 873°C for the purpose of determining the thermodynamic properties of sulphur dissolved in liquid tin. It was found that the molten tin containing sulphur is regarded as an ideal solution in the range of conditions studied. Experimental results obtained are summarized as follows:

$$\underline{S}\ (\text{in liq. Sn}) + H_2 = H_2S\,;\quad K = \frac{P_{H_2S}}{P_{H_2}\cdot[\%S]} = \frac{K_p}{[\%S]}\ ,$$

$$\log K = -\frac{2{,}397}{T} + 0.495\ ,$$

$$\Delta F^\circ = 10{,}964 - 2.264\,T\ .$$

Combining these equations with the known ones for the equilibrium constant of the formation reaction of hydrogen sulphide gas, the following approximate equations for the dissociation pressure of sulphur dissolving in molten tin between 727° and 873° C were obtained.

$$2\,\underline{S}\ (\text{in liq. Sn}) = S_2\,;\quad K' = P_{S_2}/[\%S]^2\ ,$$

$$\log K' = -\frac{14{,}180}{T} + 6.090\ ,$$

$$\Delta F^\circ = 64{,}860 - 27.86\,T\ .$$

Furthermore combining the results observed with the equilibrium constants of dissociation of hydrogen sulphide gas computed from the exact formula as a function of temperature, the values of log K' at experimental temperatures were calculated and compared with those from above equation and then it was found that both values agree with each other at each temperature.

Acknowledgement

The present writer wishes to express his cordial thanks to Prof. K. Ono, Director of the Research Institute, for his advice and encouragement, to Prof. T. Isihara for reading the manuscript with valuable criticism and to Prof. M. Kameda for his encouragement. His thanks are also due to Mr. A. Yamagishi for his zealous assistance during the course of the present work.

This work was supported in part by a grant in aid for fundamental research of the Ministry of Education.